

## CLAIMS

1. An electrochemical cell structure, comprising:
  - an anode comprising a material selected from the group consisting of active metal, active metal-ion, active metal alloying metal, and active metal intercalating material; and
  - an ionically conductive protective architecture on a first surface of the anode, the architecture comprising,
    - an active metal ion conducting separator layer comprising a non-aqueous anolyte, the separator layer being chemically compatible with the active metal, and in contact with the anode, and
    - a substantially impervious ionically conductive layer chemically compatible with the separator layer and with aqueous environments, and in contact with the separator layer.
2. The structure of claim 1, wherein the separator layer comprises a semi-permeable membrane impregnated with a non-aqueous anolyte.
3. The structure of claim 2, wherein the semi-permeable membrane is a micro-porous polymer.
4. The structure of claim 3, wherein the anolyte is in the liquid phase.
5. The structure of claim 4, wherein the anolyte comprises a solvent selected from the group consisting of organic carbonates, ethers, esters, formates, lactones, sulfones, sulfolane and combinations thereof.
6. The structure of claim 5, wherein the anolyte comprises a solvent selected from the group consisting of EC, PC, DEC, DMC, EMC, THF, 2MeTHF, 1,2-DME or higher glymes, sulfolane, methyl formate, methyl acetate, and combinations thereof and a supporting salt selected from the group consisting of LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, LiClO<sub>4</sub>, LiSO<sub>3</sub>CF<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> and LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>.
7. The structure of claim 6, wherein the anolyte further comprises 1,3-dioxolane.
8. The structure of claim 3, wherein the anolyte is in the gel phase.

9. The structure of claim 8, wherein the anolyte comprises a gelling agent selected from the group consisting of PVdF, PVdF-HFP copolymer, PAN, and PEO and mixtures thereof; a plasticizer selected from the group consisting of EC, PC, DEC, DMC, EMC, THF, 2MeTHF, 1,2-DME and mixtures thereof; and a Li salt selected from the group consisting of LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, LiClO<sub>4</sub>, LiSO<sub>3</sub>CF<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> and LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>.
10. The structure of claim 1, wherein the substantially impervious ionically conductive layer comprises a material selected from the group consisting of glassy or amorphous active metal ion conductors, ceramic active metal ion conductors, and glass-ceramic active metal ion conductors.
11. The structure of claim 10, wherein the active metal is lithium.
12. The cell of claim 11, wherein substantially impervious ionically conductive layer is an ion conductive glass-ceramic having the following composition:

Composition	mol %
P <sub>2</sub> O <sub>5</sub>	26-55%
SiO <sub>2</sub>	0-15%
GeO <sub>2</sub> + TiO <sub>2</sub>	25-50%
in which GeO <sub>2</sub>	0--50%
TiO <sub>2</sub>	0--50%
ZrO <sub>2</sub>	0-10%
M <sub>2</sub> O <sub>3</sub>	0 < 10%
Al <sub>2</sub> O <sub>3</sub>	0-15%
Ga <sub>2</sub> O <sub>3</sub>	0-15%
Li <sub>2</sub> O	3-25%

and containing a predominant crystalline phase composed of Li<sub>1+x</sub>(M,Al,Ga)<sub>x</sub>(Ge<sub>1-y</sub>Ti<sub>y</sub>)<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> where  $X \leq 0.8$  and  $0 \leq Y \leq 1.0$ , and where M is an element selected from

the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and  $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$  where  $0 < X \leq 0.4$  and  $0 < Y \leq 0.6$ , and where Q is Al or Ga.

13. The structure of claim 1, wherein the substantially impervious ionically conductive layer has an ionic conductivity of at least  $10^{-5}\text{S/cm}$ .
14. The structure of claim 1, wherein non-aqueous electrolyte separator layer has an ionic conductivity of at least  $10^{-5}\text{S/cm}$ .
15. The structure of claim 1, wherein the anode comprises active metal.
16. The structure of claim 1, wherein the anode comprises active metal-ions.
17. The structure of claim 1, wherein the anode comprises active metal alloying metal.
18. The structure of claim 17, wherein the active metal alloying metal is selected from the group consisting of Ca, Mg, Sn, Ag, Zn, Bi, Al, Cd, Ga, In and Sb.
19. The structure of claim 1, wherein the anode comprises active metal intercalating material.
20. The structure of claim 19, wherein the active metal intercalating material comprises carbon.
21. A battery cell, comprising:
  - an active metal anode;
  - a cathode structure; and
  - an ionically conductive protective architecture on a first surface of the anode, the architecture comprising,
    - an active metal ion conducting separator layer comprising a non-aqueous anolyte, the separator layer being chemically compatible with the active metal, and in contact with the anode, and
    - a substantially impervious ionically conductive layer chemically compatible with the separator layer and the cathode structure, and in contact with the cathode structure.

22. The cell of claim 21, wherein the separator layer comprises a semi-permeable membrane impregnated with a non-aqueous anolyte.
23. The cell of claim 22, wherein the semi-permeable membrane is a micro-porous polymer.
24. The cell of claim 23, wherein the anolyte is in the liquid phase.
25. The cell of claim 24, wherein the anolyte comprises a solvent selected from the group consisting of organic carbonates, ethers, esters, formates, lactones, sulfones, sulfolane and combinations thereof.
26. The cell of claim 25, wherein the anolyte comprises a solvent selected from the group consisting of EC, PC, DEC, DMC, EMC, THF, 2MeTHF, 1,2-DME or higher glymes, sulfolane, methyl formate, methyl acetate, and combinations thereof and a supporting salt selected from the group consisting of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiSO}_3\text{CF}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ .
27. The cell of claim 26, wherein the anolyte further comprises 1,3-dioxolane.
28. The cell of claim 23, wherein the anolyte is in the gel phase.
29. The cell of claim 28, wherein the anolyte comprises a gelling agent selected from the group consisting of PVdF, PVdF-HFP copolymer, PAN, and PEO and mixtures thereof; a plasticizer selected from the group consisting of EC, PC, DEC, DMC, EMC, THF, 2MeTHF, 1,2-DME and mixtures thereof; and a Li salt selected from the group consisting of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiSO}_3\text{CF}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ .
30. The cell of claim 21, wherein the substantially impervious ionically conductive layer comprises a material selected from the group consisting of glassy or amorphous active metal ion conductors, ceramic active metal ion conductors, and glass-ceramic active metal ion conductors.
31. The cell of claim 30, wherein the active metal is lithium.
32. The cell of claim 31, wherein substantially impervious ionically conductive layer is an ion conductive glass-ceramic having the following composition:

Composition	mol %

P <sub>2</sub> O <sub>5</sub>	26-55%
SiO <sub>2</sub>	0-15%
GeO <sub>2</sub> + TiO <sub>2</sub>	25-50%
in which GeO <sub>2</sub>	0--50%
TiO <sub>2</sub>	0--50%
ZrO <sub>2</sub>	0-10%
M <sub>2</sub> O <sub>3</sub>	0 < 10%
Al <sub>2</sub> O <sub>3</sub>	0-15%
Ga <sub>2</sub> O <sub>3</sub>	0-15%
Li <sub>2</sub> O	3-25%

and containing a predominant crystalline phase composed of  $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$  where  $X \leq 0.8$  and  $0 \leq Y \leq 1.0$ , and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and  $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$  where  $0 < X \leq 0.4$  and  $0 < Y \leq 0.6$ , and where Q is Al or Ga.

33. The cell of claim 21, wherein the substantially impervious ionically conductive layer has an ionic conductivity of at least  $10^{-5}\text{S/cm}$ .

34. The cell of claim 21, wherein non-aqueous electrolyte separator layer has an ionic conductivity of at least  $10^{-5}\text{S/cm}$ .

35. The cell of claim 21, wherein the anode comprises active metal.

36. The cell of claim 21, wherein the anode comprises active metal-ions.

37. The cell of claim 21, wherein the anode comprises active metal alloying metal.

38. The cell of claim 37, wherein the active metal alloying metal is selected from the group consisting of Ca, Mg, Sn, Ag, Zn, Bi, Al, Cd, Ga, In and Sb.

39. The cell of claim 21, wherein the anode comprises active metal intercalating material.

40. The cell of claim 39, wherein the active metal intercalating material comprises carbon.
41. The cell of claim 21, wherein the cathode structure comprises an electronically conductive component, an ionically conductive component, and an electrochemically active component, wherein at least one cathode structure component comprises an aqueous constituent.
42. The cell of claim 41, wherein the cathode structure comprises an aqueous electrochemically active component.
43. The cell of claim 42, wherein the aqueous electrochemically active component is water.
44. The cell of claim 42, wherein the aqueous electrochemically active component comprises a water soluble oxidant selected from the group consisting of gaseous, liquid and solid oxidants and combinations thereof.
45. The cell of claim 44, wherein the water soluble gaseous oxidants are selected from the group consisting of  $O_2$ ,  $SO_2$  and  $NO_2$ , and the water soluble solid oxidants are selected from the group consisting of  $NaNO_2$ ,  $KNO_2$ ,  $Na_2SO_3$  and  $K_2SO_3$ .
46. The cell of claim 44, wherein the water soluble oxidant is a peroxide.
47. The cell of claim 46, wherein the water soluble oxidant is hydrogen peroxide.
48. The cell of claim 41, wherein the ionically conductive component and the electrochemically active component are comprised of an aqueous electrolyte.
49. The cell of claim 48, wherein the aqueous electrolyte is selected from the group consisting of strong acid solutions, weak acid solutions, basic solutions, neutral solutions, amphoteric solutions, peroxide solutions and combinations thereof.
50. The cell of claim 48, wherein the aqueous electrolyte comprises members selected from the group consisting of aqueous solutions of  $HCl$ ,  $H_2SO_4$ ,  $H_3PO_4$  acetic acid/Li acetate,  $LiOH$ ; sea water,  $LiCl$ ,  $LiBr$ ,  $LiI$ ,  $NH_4Cl$ ,  $NH_4Br$  and hydrogen peroxide, and combinations thereof.
51. The cell of claim 50, wherein the aqueous electrolyte is sea water.

52. The cell of claim 10, wherein the aqueous electrolyte comprises sea water and hydrogen peroxide.
53. The cell of claim 50, wherein the aqueous electrolyte comprises an acidic peroxide solution.
54. The cell of claim 50, wherein hydrogen peroxide dissolved in aqueous electrolyte flowing through the cell.
55. The cell of claim 41, wherein the cathode structure electronically conductive component is a porous catalytic support.
56. The cell of claim 55, wherein the porous catalytic electronically conductive support comprises nickel.
57. The cell of claim 55, wherein the porous catalytic electronically conductive support is treated with an ionomer.
58. The cell of claim 42, wherein the cathode structure electrochemically active material comprises air.
59. The cell of claim 58, wherein the air comprises moisture.
60. The cell of claim 59, wherein the ionically conductive material comprises an aqueous constituent.
61. The cell of claim 60, wherein the ionically conductive material further comprises an ionomer.
62. The cell of claim 61, wherein the ionically conductive material comprises a neutral or acidic aqueous electrolyte.
63. The cell of claim 62, wherein the aqueous electrolyte comprises LiCl.
64. The cell of claim 62, wherein the aqueous electrolyte comprises one of  $\text{NH}_4\text{Cl}$ , and HCl.
65. The cell of claim 41, wherein the cathode structure comprises an air diffusion membrane, a hydrophobic polymer layer, an oxygen reduction catalyst, an electrolyte, and an electronically conductive component/current collector.
66. The cell of claim 65, wherein the electronically conductive component/current collector comprises a porous nickel material.

67. The cell of claim 65, further comprising a separator disposed between the protective membrane and the cathode structure.
68. The cell of claim 41, wherein the cathode structure electrochemically active component comprises a metal hydride alloy.
69. The cell of claim 68, wherein the cathode structure ionically conductive component comprises an aqueous electrolyte.
70. The cell of claim 69, wherein the aqueous electrolyte is acidic.
71. The cell of claim 70, wherein the aqueous electrolyte comprises a halide acid or acidic salt.
72. The cell of claim 71, wherein the aqueous electrolyte comprises a chloride or bromide acid or acidic salt.
73. The cell of claim 72, wherein the aqueous electrolyte comprises one of HCl, HBr,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ .
74. The cell of claim 73, wherein the metal hydride alloy comprises one of an  $\text{AB}_5$  and an  $\text{AB}_2$  alloy.
75. The cell of claim 21, wherein the cell is a primary cell.
76. The cell of claim 21, wherein the cell is a rechargeable cell.
77. The cell of claim 21, wherein the cell has a planar configuration.
78. The cell of claim 21, wherein the cell has a tubular configuration.
79. The cell of claim 41, wherein the active metal is lithium and the cathode structure comprises an aqueous ionically conductive component and a transition metal oxide electrochemically active component.
80. The cell of claim 79, wherein the transition metal oxide is selected from the group consisting of  $\text{NiOOH}$ ,  $\text{AgO}$ , iron oxide, lead oxide and manganese oxide.
81. The cell of claim 21, wherein the anolyte further comprises a monomer for a polymer that is insoluble or minimally soluble in water and the catholyte comprises a polymerization initiator for the monomer.
82. The cell of claim 81, wherein the monomer is 1,3-dioxolane.



83. The cell of claim 82, wherein the polymerization initiator comprises at least one of the group consisting of protonic acid and water soluble Lewis acids dissolved in the catholyte.

84. The cell of claim 83, wherein the polymerization initiator comprises  
5 benbenzoyl cation.

85. A method of providing for the shut down of an electrochemical cell in accordance with claim 21 in the event of structural failure comprising providing in the anolyte a monomer for a polymer that is insoluble or minimally soluble in water and in the catholyte a polymerization initiator for the monomer.

86. The cell of claim 21, wherein the cathode structure comprises an ionically conductive component.

87. The cell of claim 86, wherein the ionically conductive component comprises a non-aqueous catholyte.

88. The cell of claim 87, wherein the catholyte comprises a material selected from the group consisting of organic liquids and ionic liquids.

89. The cell of claim 88, wherein the catholyte is a solution of a Li salt in an aprotic

solvent selected from the group consisting of organic carbonates, ethers, lactones, sulfones esters, formates and combinations thereof.

90. The cell of claim 89, wherein the catholyte is selected from the group consisting of EC, PC, DEC, DMC, EMC, THF, 2MeTHF, 1,2-DME and higher glymes, 1,3 dioxolane, sulfolane, methyl formate, methyl acetate, and combinations thereof, and a supporting salt selected from the group consisting of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiSO}_3\text{CF}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  and combinations thereof.

91. The cell of claim 90, further comprising a dissolved a solid, liquid or gaseous oxidant selected from the group consisting of lithium polysulfides,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{SOCl}_2$ .

92. The cell of claim 87, wherein the catholyte comprises an ionic liquid selected from the group consisting of imidazolium derivatives, pyridinium derivatives, phosphonium compounds, and tetralkylammonium compounds, and combinations thereof.

93. The cell of claim 92, wherein the ionic liquid is selected from the group consisting of 1-Ethyl-3-methylimidazolium tosylate (EMIM-Ts), 1-Butyl-3-methylimidazolium octyl sulfate (BMIM-OctSO<sub>4</sub>), 1-Ethyl-3-methylimidazolium hexafluorophosphate, and 1-Hexyl-3-methylimidazolium tetrafluoroborate.
94. A method of making a battery cell in accordance with claim 21, comprising:
- providing the following components,
  - an active metal anode;
  - a cathode structure; and
  - an ionically conductive protective architecture on a first surface of the anode,
- the architecture comprising,
- an active metal ion conducting separator layer comprising a non-aqueous anolyte, the separator layer being chemically compatible with the active metal, and in contact with the anode, and
  - a substantially impervious ionically conductive layer chemically compatible with the separator layer and the cathode structure, and in contact with the cathode structure; and
- assembling the components.
95. The method of claim 94, wherein the substantially impervious ionically conductive layer is tubular.
96. The cell of claim 43, further comprising a PEM H<sub>2</sub>/O<sub>2</sub> fuel cell to capture hydrogen released from the cathode structure in the battery cell redox reaction.